SCIENCE FOR GLASS PRODUCTION

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NONLINEAR OPTIC NANOCOMPOSITES BASED ON OXIDE GLASSES

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The first nonlinear optic nanocomposite based on a low-melting vitreous matrix and a ferrielectric crystal has been obtained. The matrix consists of lead-borate glass and the filler is single-phase powder of ferrielectric KNbSi2O7. The quadratic optical nonlinearity of composites was studied depending on temperature and time of dissolution of crystals in the glass matrix. Conditions for producing transparent nanocomposites that generate the second optic harmonic are identified.

Interest in the development of nonlinear-optical media based on glass has significantly increased in the past few years. Quadratic optical nonlinearity, which is expressed, in particular, in the effect of second harmonic generation (SHG), is absent in normal glass due to its inversion symmetry prohibiting optical nonlinearity of even orders. This prohibition can be removed by thermal treatment of glass in a electric field [1, 2], by oriented crystallization of non-center-symmetric (NCS) phases on the glass surface [3], and by nanostructuring of glass using semiconductor, metallic, or NSC oxide crystals [4 – 7].

Furthermore, a possible way for developing nonlinear optical media based on glass is introducing nonlinear optical crystals into a vitreous melt and producing a transparent composite. The feasibility of this approach was experimentally demonstrated in [8]: nonlinear optical crystals β-BaB_2O_4 were introduced into borosilicate glass and by coordination of density and refraction indexes of the glass and crystals sized 0.5 – 2.0 μm, it was possible to obtain transparent composites with high quadratic nonlinearity.

Data on transparent composites based on glass and ferrielectric crystals are missing, despite the fact that ferrielectrics are the most promising nonlinear optic materials, in which the vector of spontaneous polarization does not necessarily coincide with the polar axis and can be oriented by an external electric field. However, ferrielectrics in glass composites until recently were predominantly used to control thermal expansion in glass solders, due to abnormal behavior of TCLE in the temperature interval of the ferrielectric phase transformation [9].

In the present study we analyzed ferrielectric crystals as promising fillers for glass composites and estimated the possibilities of the composite approach to formation of transparent nonlinear optical media.

By solid-phase reactions we synthesized a wide range of single-phase powders of high-melting and low-melting ferrielectric crystals with different optical nonlinearity: niobates of lithium, sodium, and potassium, lithium tantalate, potassium niobosilicate $KNbSi_2O_7$, stilwellites $LaBGeO_5$ and $LaBSiO_5$, as well as low-melting borates RB_4O_7 (where R are Sr and Pb) and solid solutions based on them.

All powders obtained were tested by x-ray phase analysis (a DRON-3M diffractometer, CuK_α radiation, a nickel filter) and when a single phase of the powder was confirmed, its optical nonlinearity was determined as the effectiveness of the SHG signal compared with the reference standard represented by α-quartz powder according to the method in [10]. The parameters of the ferrielectric phases and powders specified are listed in Table 1. The diversity of properties of materials listed in Table 1 provides vast opportunities for designing glass compositions and producing composites with various properties.

The vitreous matrices for composites at the initial stage of research were low-melting glasses of the system $PbO – B_2O_3$, whose properties are well known [11]. When composites are used for optics, it is desirable for the refractive indexes of the crystals to correlate with the refractive index of the matrix glass, and this can be implemented even in

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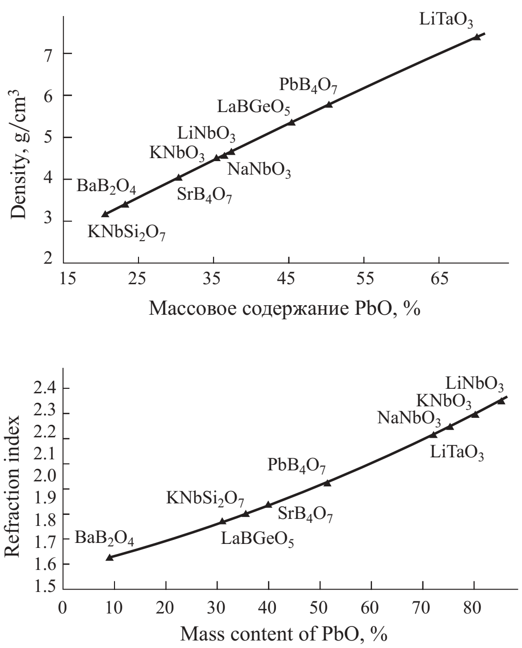

Fig. 1. Concentration dependence of density and refraction index of glass in system $PbO – B_2O_3$ [11]: ▲) values of density and refraction index for some nonlinear optic crystals.

the binary lead-borate system. The dependences of the refractive index and density of lead-borate glasses on a content of PbO published in [11] are indicated in Fig. 1. Glasses of the system $PbO – B_2O_3$ make it possible to overlap the entire variation range of the refractive index and density of nonlinear optic crystals considered, and it can be seen in Fig. 1 which glass composition ensures correlation of the refractive index and density with a particular crystal.

However, comparing the concentration dependences of the refractive index and density of lead-borate glass with data for polar crystals, a conclusion can be made that a binary system has little promise as a matrix for transparent composites. Indeed, regarding lithium, sodium, and potassium niobates and especially lithium tantalate, there is a great difference between glass compositions that ensure coordination of the refractive index and density for glasses and crystals. These crystals with respect to their refractive index correlate with a high-lead glass composition, whereas with respect to density they correlate with glass containing 35 wt.% PbO. The situation with $KNbSi_2O_7$ is more favorable: crystal $KNbSi_2O_7$ of density 3.2 g/cm^3 correlates with a glass composition containing neatly 30% PbO, on the other hand, its refractive index correlates with glass containing about 35% PbO. Clearly, such discrepancy can be eliminated by making the glass composition more complex. For instance, it makes sense to add SiO_2 and K_2O into silicate-borate glass, since it is known that introduction of K_2O into silicate glass does not raise density, but perceptibly increases the refractive index [11]. On the other side, the problem of batch stratification due to a difference in the densities of glass and crystals can be solved by adding crystals into a glass matrix cooled to a more viscous state and subjected to intense stirring (for instance, using an ultrasonic field).

In our work we have demonstrated the possibility of developing glass composites with nonlinear optic properties based on a ferroelectric crystal, taking as example ferrielectric $KNbSi_2O_7$ and glass of composition $PbO \cdot 4B_2O_3$. Ferrielectric $KNbSi_2O_7$ has high quadratic nonlinearity and relatively low density and refractive index. This crystal preserves its ferrielectric state up to its melting point. Since in the initial stage of research we were primarily interested in the fundamental possibility of obtaining a composite and the related parameter of the rate of dissolution of crystals in glass without their precipitation, we selected glass $PbO \cdot 4B_2O_3$, whose density is close to the density of the crystal.

Figure 2 shows a dependence of the SHG signal $I_{2\omega}$ on the duration of synthesis of composites with a molar content of 10% $KNbSi_2O_7$ and 90% $PbO \cdot 4B_2O_3$ at a temperature of 950°C. For the first 30 min of exposure the composites were opaque or semiopaque. As the exposure duration increased, the composites clarified and became transparent, preserving to some extent nonlinear-optic properties. A monotonically decreasing dependence of the SHG signal on the exposure duration (Fig. 2) and the data of x-ray phase analysis (Fig. 3) indicate the x-ray-amorphism of clear and semiopaque samples and suggest that crystals $KNbSi_2O_7$ dissolve to nano-scale sizes.

The data in Fig. 2 and 3 suggest that starting with a certain duration of synthesis, a nanostructure is formed in the composite, which represents nanodimensional "residues" of initial crystals and generates the second harmonic weakly descending with time. The values $I_{2\omega}$ of transparent nanocomposites obtained have the same order as

TABLE 1

Composition of nonlinear optic fillers	Syngony, structural type, spatial group	Melting point, °C	Curie point, °C	Refractive index	Intensity of SHG signal of quartz reference standard, rel. units
$LiNbO_3$	Perovskite, *R*3*c*	1253	1150	2.28	100
$NaNbO_3$	Perovskite, *Pm*3*m*	1220	200	2.20	0
$KNbO_3$	Perovskite, 4*mm*	1234	430	2.20	2400
$KNbSi_2O_7$	*P*4*bm*	1180	1080	1.75	600
$LiTaO_3$	*R*3*c*	1650	660	2.15	1300
$LaBGeO_5$	Stilwellite, $P3_1$	1250	520	1.81	12
BiB_3O_6	$P2_1$	708	–	1.78	20
PbB_4O_7	$P2_1nm$	768	–	1.91	25
SrB_4O_7	The same	970	–	1.7 – 1.8	42
$Pb_{0.7}Ba_{0.3}B_4O_7$	″	769	–	–	38
$Sr_{0.7}Ba_{0.3}B_4O_7$	″	900	–	–	2

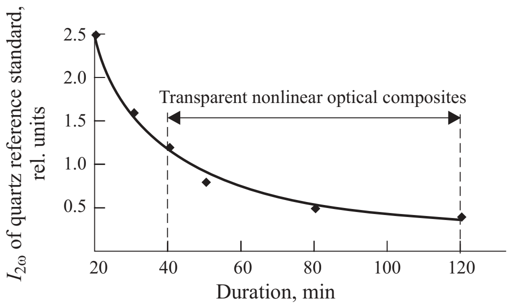

Fig. 2. Dependence of SHG signal on melting duration of composite 10% $KNbSi_2O_7$ – 90% $PbO \cdot 4B_2O_3$ at temperature of 950°C.

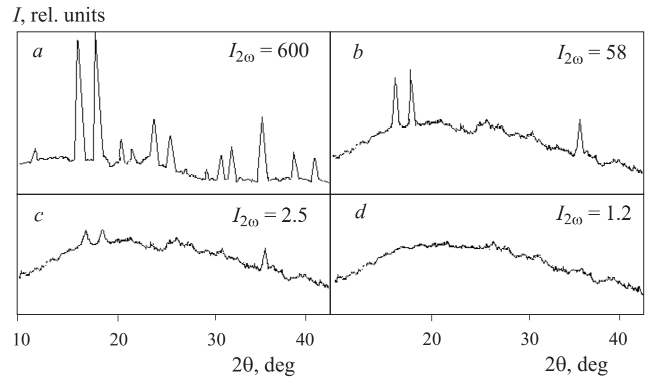

Fig. 3. Data of x-ray phase and nonlinear-optic analysis for composites based on $KNbSi_2O_7$ and glass $PbO \cdot 4B_2O_3$: *a*) single-phase powder $KNbSi_2O_7$; *b*) batch 10% $KNbSi_2O_7$ – 90% $PbO \cdot 4B_2O_3$, *c* and *d*) composite 10% $KNbSi_2O_7$ – 90% $PbO \cdot 4B_2O_3$ after heat treatment at 950°C for 20 and 40 min, respectively.

nanostructured glasses of systems $K_2O - TiO_2 - P_2O_5$ [12] and $K_2O - Nb_2O_5 - SiO_2$ [12 – 14]. Optical nonlinearity in these systems can be induced either by formation of nonlinear optic nanocrystals in glass volume (their further growth sharply increases the SHG effect), or as a consequence of spatial modulation of polarizability and the refractive index due to sedimentation of amorphous or non-center-symmetrical crystalline nanoparticles. An reverse process takes place in composites: dissolution of crystals induces optical nonlinearity according to the first mechanism in the case of sufficiently "large" crystals (over 20 – 30 nm) or (at the final dissolution stages) to a combined effect of both mechanisms, when the sizes of particles are so small that their non-center-symmetry plays a secondary role (note that usually $I_{2\omega} \sim D^4$, where D is the crystal size).

Thus, the origin of the SHG signal in composites is related either to the presence of incompletely dissolved crystals in glass, or to nanoheterogeneities in glass generated by dissolving crystals, which also produces optical nonlinearity,

To conclude, the main prerequisites for production of transparent nonlinear optic composites based on low-melting glasses can be formulated as follows:

– presence of high optical nonlinearity and a single phase in the crystalline powder selected for synthesis;

– low melting point of the matrix glass;

– leveling of refractive indexes of glass and the crystal; possibility of controlling the rate of dissolution of the crystal in glass; possibility of obtaining a glass composite without cords, bubbles, and other technological defects.

Nonlinear optic composites, in turn, can be divided into two categories: proper composites, in which micron and submicron crystals with high quadratic nonlinearity have the refractive index as close as possible to that of the matrix glass, and nanocomposites, in which the initial crystalline powder is dissolved in the glass melt to a particle size of 100 nm or less.

It is possible to achieve a high yield of the second harmonic in the first type of composites, which makes it possible to regard them as analogues of nonlinear-optic monocrystals. Due to weak dependence of $I_{2\omega}$ on exposure duration (Fig. 2), nanocomposites can be successfully used as intermediate products in drawing nonlinear-optical fiber.

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